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# Density and structural anomalies in soft-repulsive dimeric fluids<sup>†</sup>

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We report Monte Carlo results for the fluid structure of a system of dimeric particles interacting via a core-softened potential. More specifically, dimers interact through a repulsive pair potential of inverse-power form, modified in such a way that the repulsion strength is softened in a given range of distances. The aim of such a study is to investigate how both the elongation of the dimers and the softness of the potential affect some features of the model. Our results show that the dimeric fluid exhibits both density and structural anomalies even if the interaction is not characterized by two length scales. Upon increasing the aspect ratio of the dimers, such anomalies are progressively hindered, with the structural anomaly surviving even after the disappearance of the density anomaly. These results shed light on the peculiar behaviour of molecular systems of non-spherical shape, showing how geometrical and interaction parameters play a fundamental role for the presence of anomalies.

## 1 Introduction

The class of systems known as network-forming fluids, i.e. fluids characterized by intermolecular bonds strictly dependent by the orientation, has always captured great interest in the field of chemical physics. Some well-known examples of such compounds, like water<sup>1–4</sup>, carbon<sup>5</sup>, phosphorous<sup>6</sup> and silica<sup>7</sup>, have been deeply investigated because of their so-called anomalous behaviours, including re-entrant melting, diffusion and density anomalies. Water, in particular, is still object of rather intense experimental<sup>8–10</sup> and theoretical<sup>11–14</sup> investigations for its anomalous properties that deeply influence its phase behaviour, even giving rise to a possible liquid-liquid critical point. In this context, the possibility to develop simple models able to reproduce such thermodynamics anomalies even via spherically symmetric potentials constitutes a fascinating challenge; in the last years, a rich variety of models, based on some specific choices of the interaction potential, have been proposed to this aim. One of the first studies is due to Jagla<sup>15</sup>, who introduced a particular model for the intermolecular interaction by setting a short-range hard-core plus a linear repulsive shoulder at larger distances. The resulting phase diagram showed anomalous properties similar to those observed in water. The Jagla potential belongs to a more general class of intermolecular interactions called core-softened (CS) po-

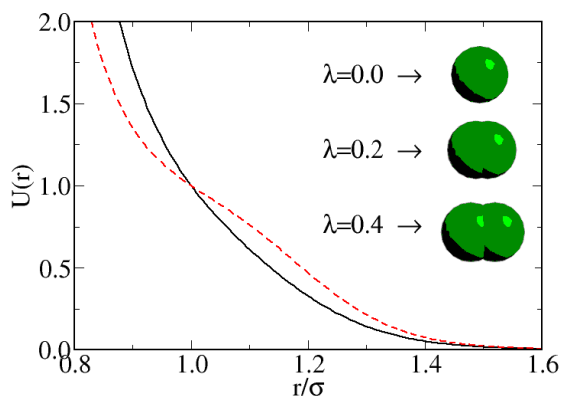
tentials: firstly introduced by Hemmer and Stell in 1970<sup>16</sup> and later recovered by Debenedetti and coworkers<sup>17</sup>, these potentials are characterized by the softening of the hard-core plus an attractive tail. It has been observed<sup>16</sup> that such a softening may cause a second transition if a first already exists. After these preliminary works, a large variety of investigations has been carried out more recently to investigate the peculiar physical properties of CS potentials: more specifically, attention has been paid to thermodynamic anomalies of the Hemmer-Stell potential<sup>18,19</sup> and of the Jagla potential<sup>20–22</sup>, as well as to liquid-liquid phase transition<sup>23–29</sup> and waterlike anomalies in CS potentials<sup>30–37</sup>. Also, CS potentials have been adopted to simulate, in a coarse-grain approach, the phase behaviour of water<sup>38</sup> and alcohols<sup>39,40</sup>.

Such interactions are characterized by two competing, expanded and compact, local arrangements of particles. This property, although arising from simple isotropic interactions, effectively mimics the behaviour of the much more complex network-forming fluids, where loose and compact local structures arise from the continuous formation and disruption of the dynamic network originated by orientational bonds. Recently, the two-scale picture as a requisite for anomalous behaviours has been challenged by some studies showing that even a weak softening of the repulsive interparticle interaction, though not able to yield two distinct length scales, may nevertheless give origin to anomalous behaviours<sup>41,42</sup>.

In this study we investigate the fluid phase of a model composed by dimeric particles interacting via a modified inverse-power potential (MIP)<sup>43</sup> by performing extensive Monte Carlo

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**Fig. 1** Site-site pair potential energy  $U(r)$  at  $\alpha = 0.6$  (full line) and  $\alpha = 0.8$  (dashed line). Cartoons of dimers upon increasing  $\lambda$  are also shown.

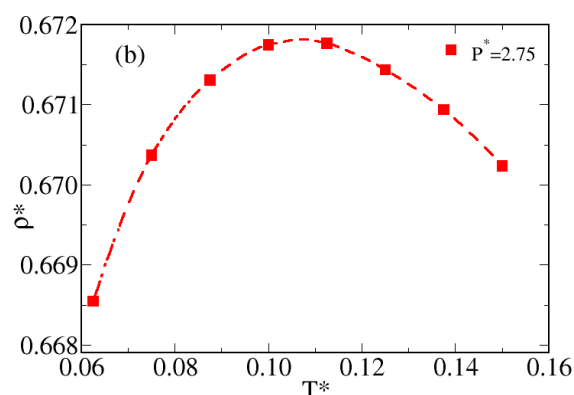
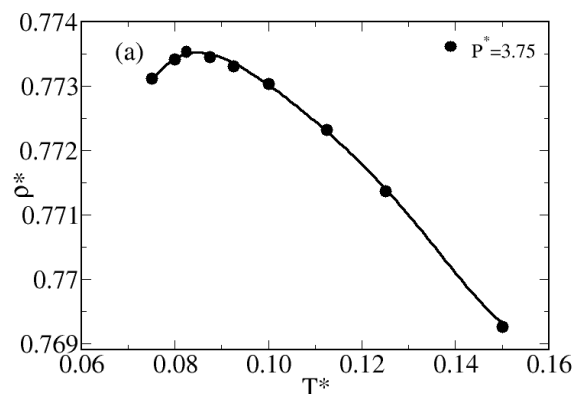
(MC) simulations in the canonical ensemble. In previous works<sup>43,44</sup> it has been shown that a system of spherical particles interacting through MIP can display typical water-like anomalies by varying carefully the softening parameter of the interparticle potential. Such an approach allows one to follow the crossover from one-scale behaviour characterizing Lennard-Jones-like fluids to a two-scale behaviour typical of CS potential systems. Here we generalize this approach by considering symmetric dimers of variable aspect ratio, modeled as two partially fused spheres interacting with the spheres of another dimer via the MIP potential. Starting with the monomeric case we progressively increase the aspect ratio with the aim to investigate how some anomalous behaviours are influenced by the red elongated shape of the molecules. At the same time, the two different conditions corresponding to one and two length scales of the potential are taken into account. In a previous study by de Oliveira and coworkers<sup>45</sup> the authors studied a model consisting of dimeric molecules which interact through an intermolecular continuous shoulder potential, but they limited their analysis to a single value of the aspect ratio.

The novelty of our study relies in the attempt to relate both the geometry of the system and the specific form of the interaction potential to the onset of anomalies in molecular non-spherical fluids, with a possible application to a wide range of soft systems.

The paper is organized as follows: in the next section we provide details of the model and the simulation approach. Results are presented and discussed in the third section and conclusions follow in the last section.

## 2 Model and simulations

The sequence of models investigated in this work is schematically depicted in Fig. 1: starting from two spheres totally overlapped we progressively increase the distance from their centres, decreasing the overlapping volume. In this way we obtain dimers comprised by two spherical particles rigidly bonded together. If we indicate the aspect ratio  $\lambda$  as the distance between the two



**Fig. 2** Density versus temperature at constant pressure for  $\alpha = 0.6$  and  $\lambda = 0.05$  (a) and for  $\alpha = 0.8$  and  $\lambda = 0.20$  (b).

centers of the spheres, we move from  $\lambda = 0$  (total overlap) to  $\lambda = 0.40$ . In this range, each value attained by  $\lambda$  is smaller than the radius  $\sigma/2$  of the spheres constituting the dimers ( $\sigma$  being the diameter). The interaction site-site potential is set as:

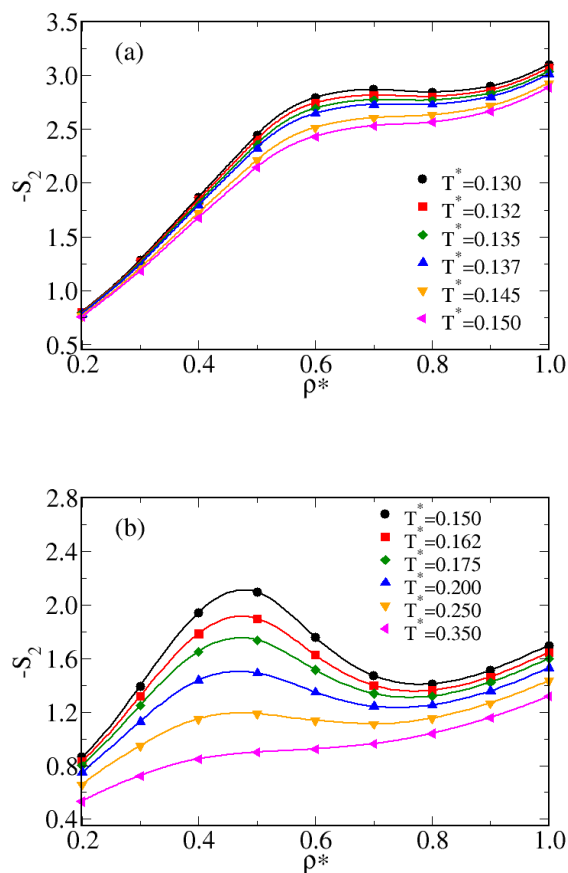
$$U(r) = \varepsilon(\sigma/r)^{n(r)} \quad (1)$$

where  $\varepsilon$  and  $\sigma$  are the units of energy and length, respectively, and

$$n(r) = n_0 \{1 - \alpha \exp[-b(1 - r/\sigma)^2]\} \quad (2)$$

In this equation,  $\alpha$  is a real number between 0 and 1 and  $b$  and  $n_0$  are positive integer numbers. Also, we define reduced temperature, density and pressure as, respectively,  $T^* \equiv k_B T/\varepsilon$ ,  $\rho^* \equiv \rho \sigma^3$  and  $P^* \equiv P \sigma^3/\varepsilon$ , where  $k_B$  is the Boltzmann constant.

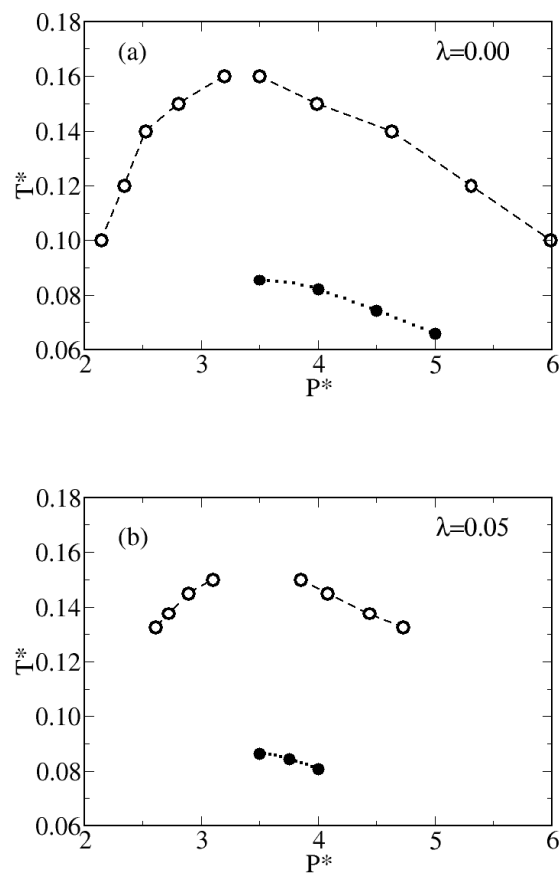
In Eqs. 1-2, introduced and investigated in Refs.<sup>43,44</sup>,  $\alpha$  takes into account the repulsion softening, while  $b$  controls the width of the interval where  $n(r)$  is smaller than  $n_0$ . In the following, we keep fixed  $b = 5$  and  $n_0 = 12$  and investigate the two different cases corresponding to  $\alpha = 0.6$  and  $\alpha = 0.8$ . The behaviour of  $U(r)$  for these two cases is also reported in Fig. 1: one can notice that for  $\alpha = 0.6$ , the potential essentially follows an inverse-power law, whereas for  $\alpha = 0.8$  there is an inflection point with



**Fig. 3** Pair translational entropy  $S_2$  as a function of the density along several isotherms for  $\lambda = 0.1$  and  $\alpha = 0.6$  (a) and  $0.8$  (b).

a change of the concavity. As demonstrated in a previous work on monomeric particles interacting via the same potential of the model at issue<sup>43</sup>, for  $\alpha = 0.6$  the potential exhibits one length scale, whereas for  $\alpha = 0.8$  two distinct, repulsive length scales emerge, giving rise to a competition between them. The condition  $\lambda < \sigma/2$  ensures that the effective global dimer-dimer interaction preserves the same features of the site-site potential in terms of one or two length scales.

In order to investigate the fluid structure and to ascertain the presence of possible anomalies of this system, we have carried out standard Monte Carlo (MC) simulations in the NVT ensemble. We have kept fixed the total number of dimers ( $N = 864$ ) enclosed in a cubic box with periodic boundary conditions. As for the simulation runs, for each investigated value of  $\lambda$  we have first performed a series of simulations at relatively high temperatures (specifically  $T^* = 0.40$ ) upon progressively increasing the density from 0.2 to 1.0. Once obtained the equilibration, we have gradually cooled the system with a  $\Delta T$  step of 0.05. For each run we have performed  $2 \times 10^5$  steps to equilibrate the system, then followed by the same number of steps to collect statistical properties. At low temperatures we have extended the number of steps up to  $5 \times 10^5$  in order to ensure a proper equilibration even in such conditions.



**Fig. 4** Loci of structural (open symbols) and density (full symbols) anomalies in the pressure-temperature plane at  $\alpha = 0.6$  upon increasing  $\lambda$ .

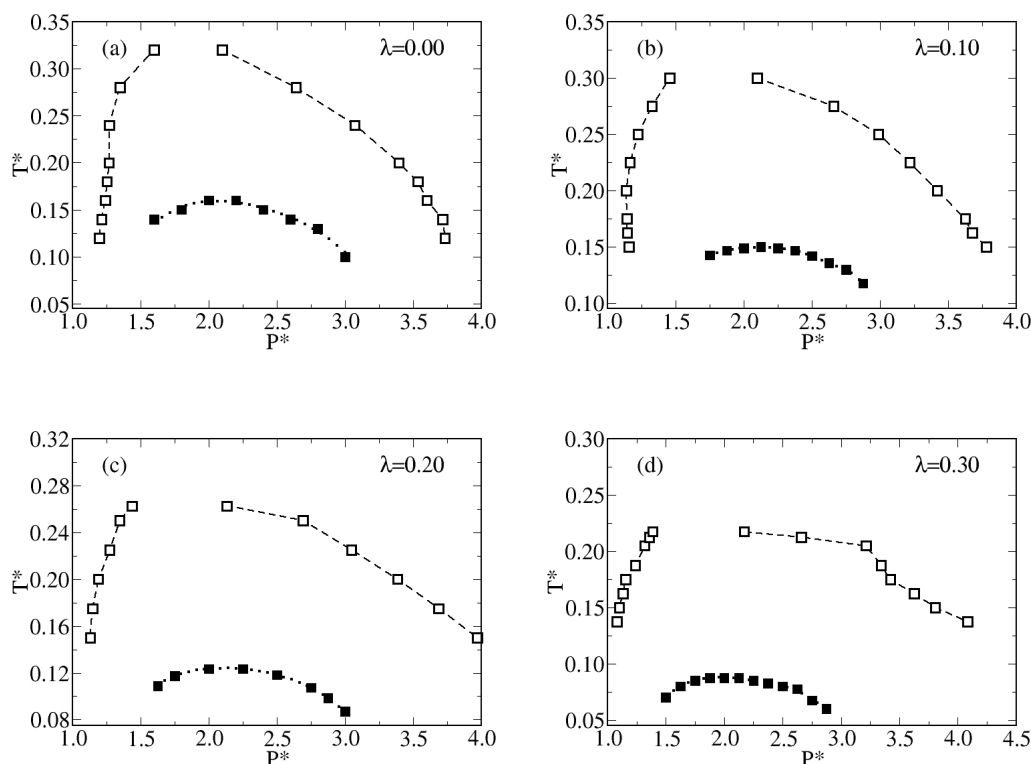
### 3 Results

We first remind that in the monomeric case, corresponding to  $\lambda = 0$ , density and structural anomalies have been observed for both  $\alpha = 0.6$  and  $\alpha = 0.8$ <sup>43,44</sup>. The density anomaly indicates an unusual expansion of the system upon cooling, with the density increasing till to reach a maximum and then decreasing. The structural anomaly is instead characterized by the unusual behaviour of the pair translational entropy  $S_2$  defined as<sup>46</sup>:

$$S_2/k_B = -\frac{1}{2}\rho \int d\mathbf{r} [g_{cm}(r) \ln g_{cm}(r) - g_{cm}(r) + 1] \quad (3)$$

where  $g_{cm}(r)$  is the pair distribution function between the centers of mass of two dimers. This quantity effectively characterizes the degree of pair translational order present in the fluid<sup>47</sup>. At variance with a simple fluid,  $-S_2$  has a non-monotonic behaviour for systems interacting through a CS potential.

The presence of these anomalies for both the values of  $\alpha$  in the monomeric case suggests that the onset of anomalous behaviours in MIP fluids is not strictly connected with the double length scale of the potential (attained at  $\alpha = 0.8$ ) but it may be found even if the potential exhibits only one length scale (as, for instance, at



**Fig. 5** Loci of structural (open symbols) and density (full symbols) anomalies in the pressure-temperature plane at  $\alpha = 0.8$  upon increasing  $\lambda$ .

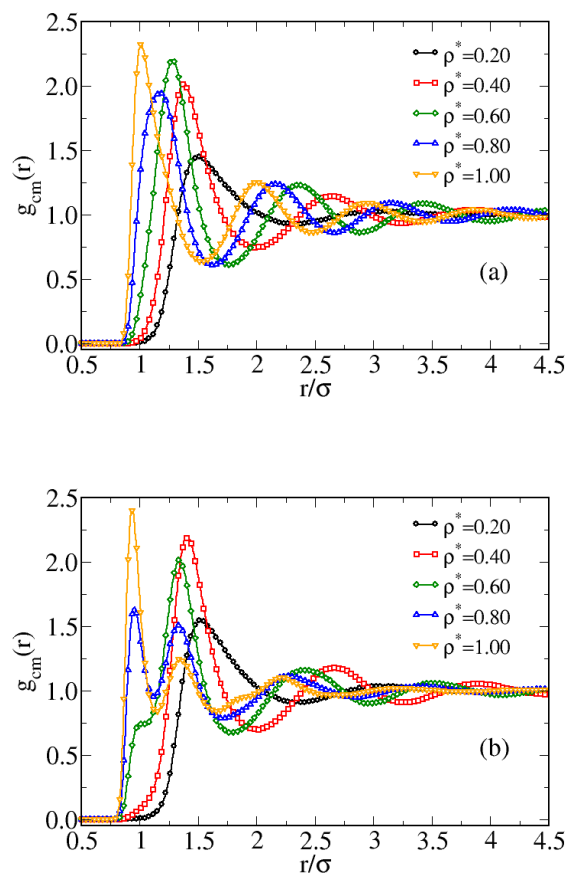
$\alpha = 0.6$ ). However, in the latter case, anomalies are more difficult to find and very extensive and careful simulations need to be performed to locate them. The effect of increasing  $\lambda$  is expected to further influence the structural and thermodynamic behaviour of the system; we shall see in the follow how the balance between aspect ratio and length scales of the potential is responsible of the onset or disappearance of anomalous behaviours in MIP dimer fluids. Also, following the prescription suggested by de Oliveira and coworkers in their previous investigation of waterlike anomalies in dimer systems<sup>45</sup>, pressure and temperature shall be rescaled by a factor of 4 if  $\lambda \neq 0$ . This is to guarantee a better comparison with the monomeric case ( $\lambda = 0$ ), where the effective intermolecular interaction between particles is four times weaker.

We report in Fig. 2 the behaviour of the density as a function of the temperature at a given pressure; more specifically, we show results for  $\alpha = 0.6$ ,  $\lambda = 0.05$  and  $P^* = 3.75$  in panel (a), while data for  $\alpha = 0.8$ ,  $\lambda = 0.2$  and  $P^* = 2.75$  are reported in panel (b). Both the two curves display a maximum of  $\rho^*$  upon increasing  $T^*$ , followed by a rapid decay; this scenario testifies the presence of a temperature of maximum density (TMD), whose value is strictly dependent on the particular pressure considered. We anticipate that the increase of  $\lambda$  tends to hinder the development of this density anomaly; specifically, the higher values of  $\lambda$  where a TMD is still observed are 0.05 for  $\alpha = 0.6$  and 0.30 for  $\alpha = 0.8$ .

Results for the pair translational entropy as a function of the

density for  $\alpha = 0.6$  and  $0.8$  at the same  $\lambda = 0.1$  are reported, respectively, in panels (a) and (b) of Fig. 3. At high values of  $T^*$ ,  $S_2$  monotonically increases with  $\rho^*$  and no anomalies are observed. Upon decreasing the temperature, the behaviour of  $S_2$  ceases to be monotonic and shows the presence of a maximum and a minimum more and more structured. This feature is clear especially for  $\alpha = 0.8$  (Fig. 3b) but it is observed, albeit in a less extent, for  $\alpha = 0.6$  also (Fig. 3a). The non-monotonic behaviour of  $S_2$  is usually related to the presence of a structural anomaly in the fluid<sup>48</sup>; as a consequence, such a kind of anomaly, already observed for both  $\alpha = 0.6$  and  $\alpha = 0.8$  in the monomeric case, survives for  $\alpha = 0.6$  even if  $\lambda = 0.1$ , where the density anomaly is disappeared.

The specific values of maxima and minima define a portion of the temperature-pressure plane corresponding to the structural anomaly region. At the same time, values attained by TMD define, in the same plane, the density anomaly region. In Fig. 4 we show these two regions for  $\alpha = 0.6$  and  $\lambda = 0$  (a) and  $\lambda = 0.05$  (b). As visible, the small increase of  $\lambda$  is enough to shrink both structural and density anomaly regions. Actually, a maximum and a minimum in  $S_2$  can be hardly detected for  $\lambda = 0.05$  if  $T^* < 0.13$ ; this is due to the development of solid-like features in  $g_{cm}(r)$  that cause a sharp increase of the correspondig pair translational entropy. As a consequence, the profile of  $S_2$  vs  $\rho^*$  shows discontinuities preventing the detection of maxima and minima in these functions. These circumstances suggest that the shrink of anomalies regions



**Fig. 6** Radial distribution functions between the centers of mass at  $T^* = 0.15$  for  $\alpha = 0.6$  and  $\lambda = 0.05$  (a) and for  $\alpha = 0.8$  and  $\lambda = 0.10$  (b) upon increasing  $\rho^*$ .

may be ascribed to an increase of the solid region with respect to the monomeric case.

Regions of structural and density anomalies for  $\alpha = 0.8$  at various  $\lambda$  are reported in Fig. 5. The effect of increasing the aspect ratio is now reflected in the lowering of the temperature where the anomalies are observed. That is, the dimer system needs to be more and more cooled before showing anomalous behaviour; if  $\lambda > 0.3$ , the density anomaly is no more observed, whereas the structural anomaly, which develops at higher temperature, is still found.

Finally, the fluid structure of MIP dimers is investigated in Fig. 6, where results for  $g_{cm}(r)$  as a function of the density for  $T^* = 0.15$  and  $\alpha = 0.6$  (a) and  $0.8$  (b) are reported. When the potential exhibits only one length scale (panel (a)), the progressive increase of  $\rho^*$  causes the shift of the first peak of  $g_{cm}(r)$  towards low values of  $r/\sigma$ . This is due to the lower typical distance between two dimers ( $\lambda = 0.05$  in this case) when the system is compressed. A different behaviour is observed for  $\alpha = 0.8$  and  $\lambda = 0.1$  (panel (b)): now, a double peak is clearly observed in  $g_{cm}(r)$  if  $\rho^* \geq 0.60$ . This feature is due to the presence of a double length scale in the potential, actually attained for  $\alpha = 0.8$ . In this case,

**Table 1** Overall behaviour of density and structural anomalies upon varying  $\alpha$  and  $\lambda$ .

$\alpha$	$\lambda$	TMD	Structural Anomaly
0.6	0.00	✓	✓
0.6	0.05	✓	✓
0.6	0.10	✗	✓
0.8	0.00	✓	✓
0.8	0.10	✓	✓
0.8	0.20	✓	✓
0.8	0.30	✓	✓
0.8	0.40	✗	✓

two distinct arrangements between dimers become possible, with the one corresponding to the first peak in  $g_{cm}(r)$  more favored upon increasing the density. However, despite the differences in the  $g_{cm}(r)$ , structural and density anomalies are both observed in the two thermodynamic state points considered in Fig. 6 (see Fig 4 and Fig 5).

The overall behaviour of these anomalies as a function of  $\alpha$  and  $\lambda$  is schematically summarized in Table 1: in particular, the effect of progressively increase the aspect ratio when the potential has one or two length scale is enlightened, at the same time enhancing the persistence of the structural anomaly when TMD disappears.

## 4 Conclusions

We have investigated the fluid phase of a model of dimers interacting through a core-softened potential by means of Monte Carlo simulations with a particular focus on their density and structural anomalies. Specifically, two dimers interact via a modified inverse-power potential (MIP), i.e. a repulsive potential of inverse-power form modified to soften the repulsion strength in a range of distances. We have considered two different conditions, corresponding to one ( $\alpha = 0.6$ ) and two ( $\alpha = 0.8$ ) length scales of the intermolecular potential, analyzing how the increase of the aspect ratio  $\lambda$  of the dimers influences their anomalous behaviour. In the spherically-symmetric case (i.e.  $\lambda = 0$ ) density and structural anomalies have been observed in both cases already in previous works<sup>43,44</sup>: here we have found that a small increase of  $\lambda$  (from 0 to 0.05) allows for the persistence of such anomalies at  $\alpha = 0.6$ . Upon further increasing  $\lambda$ , the density anomaly disappears, whereas the structural anomaly is still found for  $\lambda = 0.10$ . As for the two-length scale case, both anomalies survive till to  $\lambda = 0.30$ ; beyond this value, no density anomaly is observed, with the structural anomaly persisting for  $\lambda = 0.40$ .

The fluid structure of MIP dimers has been investigated through the radial distribution function  $g_{cm}(r)$  that shows different behaviours for the two investigated values of  $\alpha$ . In particular, the development of a double-peak structure for  $\alpha = 0.8$  is strongly reminiscent of the two-length scale of the intermolecular potential. Such a feature is not observed for  $\alpha = 0.6$ , even if density and structural anomalies are present. These findings suggest that the development of such anomalies in CS systems is not strictly dependent on the double length scale of the potential; moreover

the increase of the aspect ratio of the dimers tends to suppress the anomalies in a way depending on the specific combination of  $\alpha$  and  $\lambda$ .

Our results pave the way for a more general investigation of CS non-spherical systems, enlightening the role played by the anisotropy in affecting their phase behaviour. Such systems may include, for instance, elongated molecules, polymers and colloidal dimers, whose experimental realization<sup>49,50</sup> along with theoretical models<sup>51,52</sup> are currently object of increasing interest.

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